# X-Ray Fluorescence Spectroscopy of Metal Sulfides

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The S $K_\alpha$ spectra of the sulfur compounds were measured. The S $K_\alpha$ energies of metal sulfides were less than that of the pure sulfur in accordance with the theoretical prediction. The S $K_\alpha$ shift for CaS ($-0.239$ eV) is the largest among those of metal sulfides examined in this study. In the sulfur+selenium binary mixtures, the S $K_\alpha$ energy goes more negative than that of sulfur with increasing the selenium content. These results can be interpreted in terms of the electronegativity of the counter atoms.

The study of physico-chemical properties of non-crystalline solids has grown into one of the important fields of solid state chemistry. Various materials of this class have been studied extensively as to their thermodynamic, structural, and electrical properties.[1] In these materials all long-range order is destroyed and many of the experimental techniques for investigating structural details of crystals become of no use. However, optical spectra often remain similar if the short-range order does not change much. X-Ray emission spectroscopy might be one of the powerful means as well for exploring the short range and electronic structure.[2,3] For example, the energy of inner levels, though not participating in the chemical bonds, slightly changes depending on the valence electron configuration. Thus, the wavelengths of the X-rays due to the transitions of electrons between inner levels of an atom change from compound to compound. This is called the chemical shift of the X-ray energy. X-Ray emission studies for sulfur compounds have been examined extensively by many authors.[4–8] In the present study, a two-crystal spectrometer was applied for the close examination of the chemical shifts of metal sulfides, since they have not been surveyed as extensively as the other sulfur compounds. The sulfur + selenium amorphous mixtures were also examined. The way of analysis proposed in this paper will easily be applicable to other elements like Al, Si, and P, which are the main constituents of the inorganic amorphous materials like silicate glasses.

## Experimental

The sulfur $K_\alpha$ emission spectra were obtained by the X-ray excitation method. The spectrometer used in this experiment is of the two crystal type (Toshiba Elec. Co. AFV-701).[9] The conditions for the measurements are listed in Table 1. The angle $2\theta$ was scanned repeatedly to gain the spectra of an appropriate intensity. Pulses from the gas flow-proportional counter were stored in a multichannel analyzer and recorded on a paper tape. In order to minimize an error due to the thermal expansion of the analyzing crystals the measurement was performed in an air controlled room. For the sake of calibration, the same procedure as on the samples was performed on the reference material (orthorhombic sulfur) both before and after every measurement.

In Fig. 1 the upper parts of the sulfur $K_\alpha$ spectra of pure sulfur and CaS are shown as an example. The interval between neighboring points was 0.01 eV in this case. It is seen that $K_{\alpha_1}$ and $K_{\alpha_2}$ peaks overlap; the latter appears on a shoulder of the former one. However one easily sees a considerable shift between the maximum points of the two spectra.

Table 1. Conditions for the measurement of S $K_\alpha$ spectra

| | |
|---|---|
| X-Ray tube | Cr |
| voltage | 50 kV |
| current | 30 mA |
| Analyzing crystal | Ge(111) ($2d$=6.533 Å) |
| Detector | PR Gas, Proportional counter |
| PHA | differential |
| Scan range ($2\theta$) | 110.66—110.80° |
| Scan speed ($2\theta$) | 0.02°/min |
| Storing time interval | 2 s/channel, scan |
| Number of repeated scans | 4—5 |

In order to seek the maximum point of the spectrum, we postulated that the least square curve fit by a fourth order equation of energy can be applied to 120 intensity values (points) in the uppermost part of the spectrum, as shown in Fig. 1. The root mean square per cent deviation, $\sigma_p$, of the curve fit for the above S and CaS were 0.66 and 0.85% respectively.[†] The chemical shift was evaluated from the energy of the maximum referred to that of the orthorhombic sulfur.

The alkaline earth sulfides were prepared by heating the corresponding carbonates in a dry $H_2S$ stream at about 1000 °C. The sulfur+selenium mixtures were prepared by melting the desired quantities of sulfur and selenium in an evacuated glass ampoule and quenching it to the room temperature. The other compounds of commercial source were of reagent grade. These were ground and pressed into pellets of 34 mm diameter inside a poly-vinyl chloride ring.

## Results and Discussion

In Table 2 are given the energy differences of sulfur $K_\alpha$ of several sulfides, sulfur + selenium mixtures, and sulfate referred to that of pure sulfur. The error limits were estimated by a t-distribution method which was applied to several measurements, shown in parentheses. The literature values are also included in the table. Contamination with sulfate was detected in SrS and BaS.[††] In sulfur + selenium the absolute values

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[†] $\sigma_p = 100 \times [\sum(y_i/y_i(\text{calcd}) - 1)^2/(n-1)]^{1/2}$

[††] The contamination of sulfates causes large errors in the $K_\alpha$ shifts of sulfur in metal sulfides, because the $K_\alpha$ shifts of sulfates are large and opposite in direction. This contamination can be checked spectroscopically by examining the $K_\beta$ spectra of sulfur. In the sulfate the so-called $K_\beta'$ satellite peak appears at the lower energy side of the main peak. The intensity of the S $K_\beta'$ peak of sulfates is about 20—30% of that of the main $K_\beta$ peak. The detection of the sulfate by this satellite spectrum is useful, because it does not appear in the metal sulfides. Quantitative analysis, however, cannot be accomplished by this method.

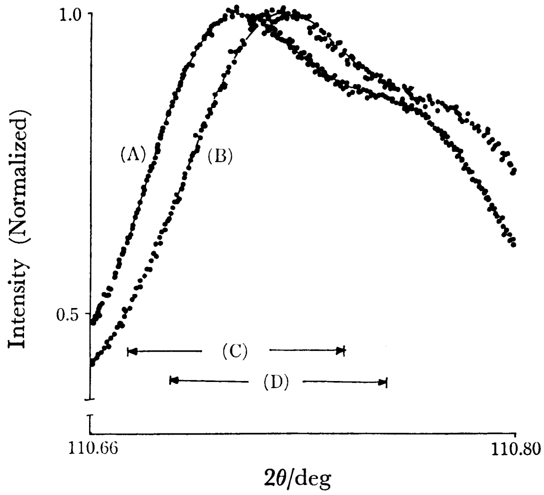

Fig. 1. Sulfur $K_\alpha$ spectra of pure sulfur and CaS (upper part only). The solid line is obtained by a least square fit of a fourth order equation of energy. (A), sulfur; (B), CaS; (C) and (D), ranges used in the least square. Maximum intensity; 28000 and 14000 counts for S and CaS respectively.

of the shifts are very small compared with those of the metal sulfides. It is seen, however, that the shift of S $K_\alpha$ became more negative with increase of the selenium content.

*Data Treatment.* Before considering the results, some discussion will be necessary about the data treatment employed in this work. The determination of the peak position is very difficult. However, the use of computer calculations on repeatedly stored data can avoid the complexity inherent to the graphical method. Among many proposed ways, the method in which the peak position is decided by the middle point of the half maximum is simple, but it requires the full spectrum and causes some uncertainties when the intensity is small. The most severe difficulty arises when the spectrum is not symmetric, as is observed in the present S $K_\alpha$ spectrum, where $K_{\alpha_1}$ and $K_{\alpha_2}$ overlap. Thus in order to seek the peak position of each component strictly, it is necessary to separate the curve into two by assuming appropriate functions, say Gaussian or Lorentzian. This procedure, however, has some mathematical complexity and gives rise to an additional uncertainty in the possible analysis. Now in the case where only the energy differences rather than the absolute values are required, almost identical results are expected to be obtained independent of the different mathematical procedures, provided the shapes of the spectra do not change as in the present case. Thus the curve fit by a polynomial equation without a process of the peak separation can also be used for the determination of the energy differences among the spectra. The parabolic fit was employed in some references.[10] However, in the spectrum obtained in this work, it is questionable whether the data can be fit by a parabola even in the top region. Actually, the range which can be approximated by a parabolic equation is restricted to the uppermost part of the spectrum and the number of points used is too small to produce a better fit. The present curve which is fit by a fourth order equation seems to be acceptable judging from the per cent deviation of the curve fit.

Table 2. Sulfur $K_\alpha$ shifts for several compounds and sulfur+selenium mixtures
$\Delta E = E(\text{specimen}) - E(\text{S})$

| Specimen | $\Delta E$/eV This work | | [1][a] | [2][b] |
|---|---|---|---|---|
| ZnS | $-0.208\pm0.005$[c] | (10)[d] | $-0.1$ | — |
| CdS | $-0.171\pm0.010$ | (11) | $-0.3$ | $-0.12$ |
| PbS | $-0.161\pm0.006$ | (10) | — | — |
| $Sb_2S_3$ | $-0.160\pm0.003$ | (10) | $-0.2$ | $-0.16$ |
| $Ag_2S$ | $-0.117\pm0.006$ | (10) | — | $-0.12$ |
| FeS | $-0.160\pm0.005$ | (10) | $-0.2$ | $-0.14$ |
| BaS[e] | $-0.201\pm0.005$ | (3) | — | $-0.14$ |
| SrS[e] | $-0.216\pm0.005$ | (3) | — | — |
| CaS | $-0.239\pm0.005$ | (8) | $-0.2$ | $-0.22$ |
| $FeSO_4$ | $+1.18$ | (2) | | |
| Sulfate (av) | — | | $+1.0$ | $+1.18$ |
| S(5)-Se(95)[f] | $-0.033\pm0.005$ | (3) | | |
| S(10)-Se(90) | $-0.027\pm0.005$ | (3) | | |
| S(25)-Se(75) | $-0.024\pm0.012$ | (3) | | |

a) Sato *et al.*, Ref. 4. b) Nefedow, Ref. 5. c) Error limit: t-distribution, 95% certainty. d) Number of measurements. e) Small contaminations of sulfate were detected in the present samples. f) Mol per cent of selenium.

*Metal Sulfides.* As stated previously, metal sulfides have not been thoroughly studied as to the S $K_\alpha$ line, because the chemical shift is not so distinct from one sulfide to the other, compared with the sulfide-sulfur-sulfite-sulfate series. The data of Sato *et al.* and of Nefedow are to be compared with the present results. The general agreement is satisfactory, although the precision was greatly improved in the present study. It is to be noted that any contamination of sulfate makes the negative shift less; some literature values of smaller shift might be explained by this reason. The same reasoning may be applicable to the values of SrS and BaS (in comparison with that of CaS).

Coulson and Zauli proposed an equation combining the chemical shifts and the partial charges on the sulfur atoms.[7] The energy shifts were expressed by a parabolic equation

$$\Delta E\, K_\alpha/\text{eV} = q(q+3)/8,$$

where $q$ is the partial charge on the sulfur. Thus the $K_\alpha$ lines of sulfur shift to the lower energy side with an accumulation of electrons on the sulfur atoms, while in sulfates and sulfites the positive shifts were predicted. As is easily seen from the above equation, the magnitudes of the negative shifts, which were expected for the metal sulfides, are very small. Thus the previous authors mainly discussed the shifts for sulfates or sulfites, in which the shifts are large and can be detected comparatively easily.

In Fig. 2 the relation between the $K_\alpha$ energy shifts from this work and Pauling's electronegativity of the counter atoms are plotted.[11] It is seen that the negative shifts increase with decrease in the electronegativity of the metals. Since the electronegativity difference

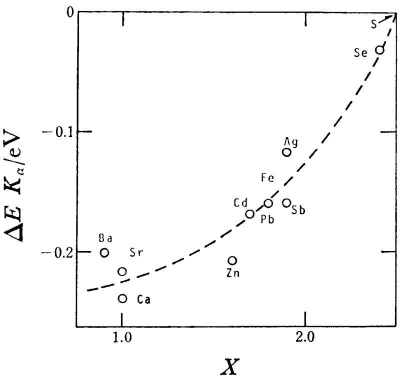

Fig. 2. Relation between S $K_\alpha$ energy shifts of metal sulfides ($\Delta E\ K_\alpha$) and Pauling's electronegativities of the counter metals ($X$). The shift at the lowest sulfur content of S+Se mixture is also included.

gives the ionicity of a bond as a first approximation, the shifts are more negative with increasing negative partial charges on the sulfur atoms. Thus it is concluded that the above theoretical equation can also be applicable to the metal sulfides. For an estimation of absolute values, however, there are some difficulties. In the condensed state the partial charges are not determined by the electronegativity difference alone. Further, since the above theoretical equation was based on the free ion model, it is not plausible to apply it straightforwardly to the estimation of the absolute charges in real crystals.

*Sulfur + Selenium.* Sulfur and selenium are quite similar elements. The Pauling's electronegativity of sulfur (2.5) is somewhat larger than that of selenium (2.4), while selenium is more electronegative by the Sanderson's scale.[12] Our previous enthalpy measurement of the liquid binary S + Se solution shows that the enthalpy is positive at all compositions and is symmetric.[13] The positive values of the enthalpy imply that the electrochemical effect is small, if present.[14] The present results show that if the chemical shifts are caused mainly by the partial charges on the sulfur atoms, sulfur bears some negative charges in the binary mixture. Further, if it is accepted that the direction of the charge transfer can be determined mainly by the electronegativity difference, the electronegativity of sulfur is larger than that of selenium, in accordance with Pauling. In the present samples quenched from the liquid state, sulfur and selenium are expected to mix randomly to form various co-rings and co-chains, as in the liquid mixture. In the dilute solution of sulfur, each sulfur atom is coordinated mainly by selenium atoms. Accordingly the electron transfer to sulfur from selenium is relatively large and the shifts are bigger at lower sulfur content, as is found (see Table 2). The shift at the lowest sulfur content was plotted in Fig. 2. As judged from the present results, the Pauling's scale is superior to the Sanderson's scale of electronegativity, although the latter is concerned with a condensed state and should be better applicable to the present system, compared with the former which is strictly applicable only to diatomic gas molecules.

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